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(56) Documents Cited

GB 2296807 A EP 0661287 A1 WO 95/24454 A1

(58) Field of Search

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(54) Thermochromic polymerizable mesogenic composition containing both chiral & achiral polymerizable mesogenic compounds & a photoinitiator, & polymers therefrom

(57) These are disclosed (1) a thermochromic polymerizable mesogenic composition essentially consisting of

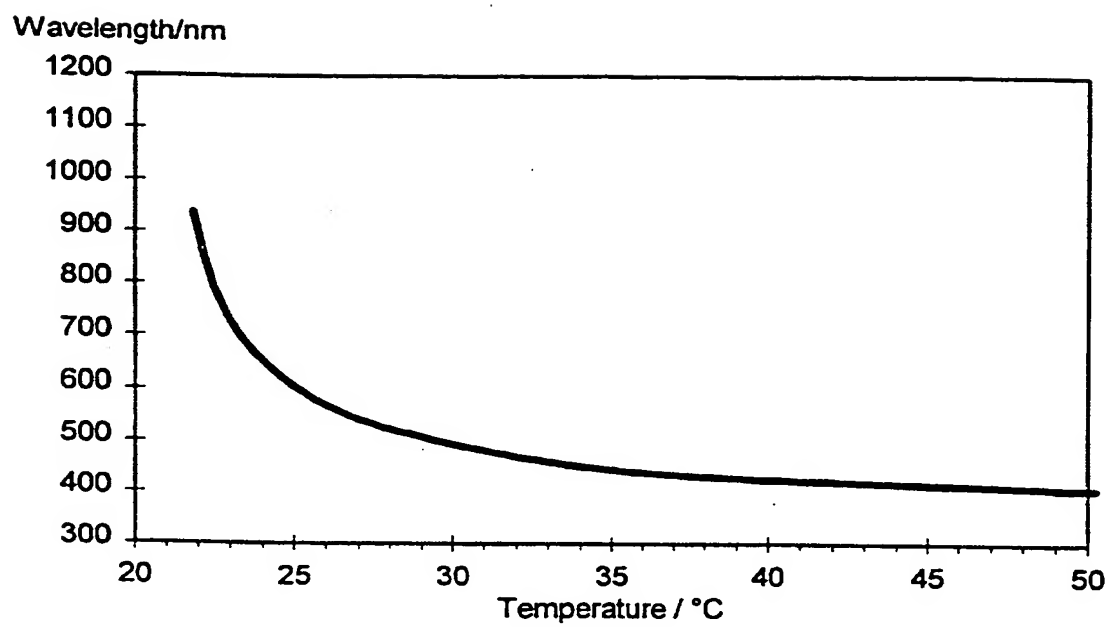
- a) a component MA comprising at least one achiral polymerizable mesogenic compound comprising at least one polymerizable functional group,
- b) a component MB comprising at least one chiral polymerizable mesogenic compound comprising at least one polymerizable functional group,
- c) a photoinitiator, and
- d) optionally a dye component,

(2) anisotropic polymers and polymer films with a chiral mesophase obtainable from said thermochromic polymerizable mesogenic composition and (3) the use of said thermochromic polymerizable mesogenic composition, anisotropic polymers and polymer films for optical information storage, photomasks, decorative pigments, cosmetics, security applications, active and passive optical elements such as polarizers or optical retarders, colour filters, scattering displays, adhesives or synthetic resins with anisotropic mechanical properties.

The polymerizable composition is thermochromic, ie shows a change of colour upon temperature variation. By polymerizing at a particular temperature, a selected reflected wavelength band can be obtained and subsequently "fixed" in the material by polymerization.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

GB 2 315 760 A

**Figure 1.1**

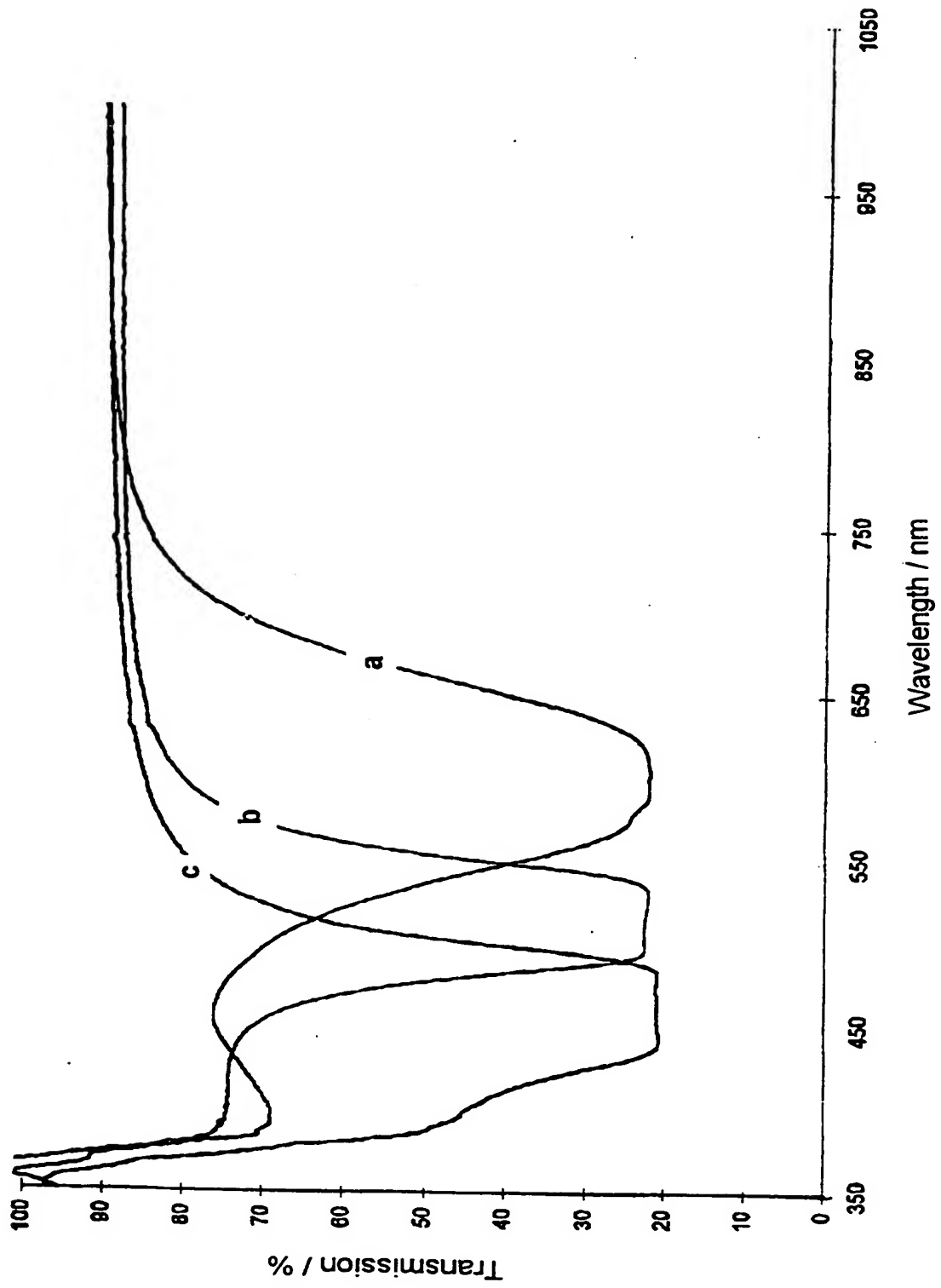
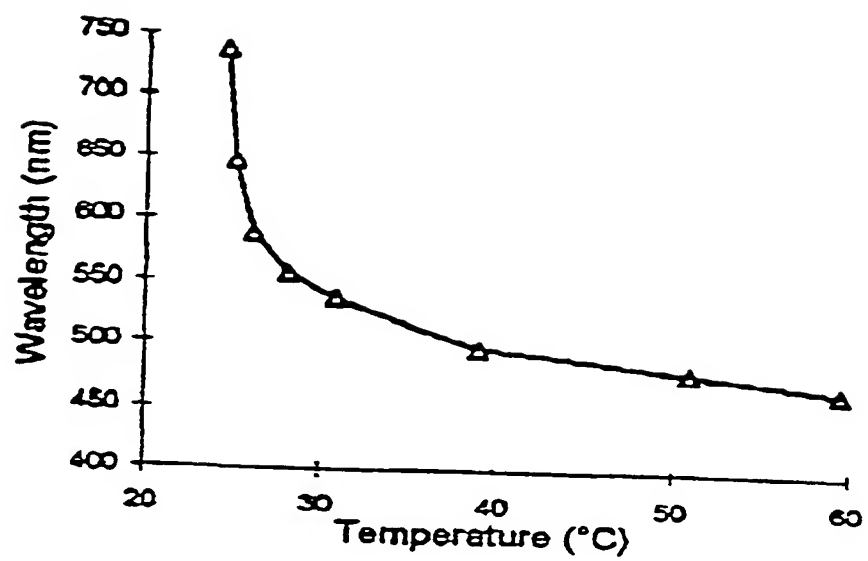


Figure 1.2

**Figure 2**

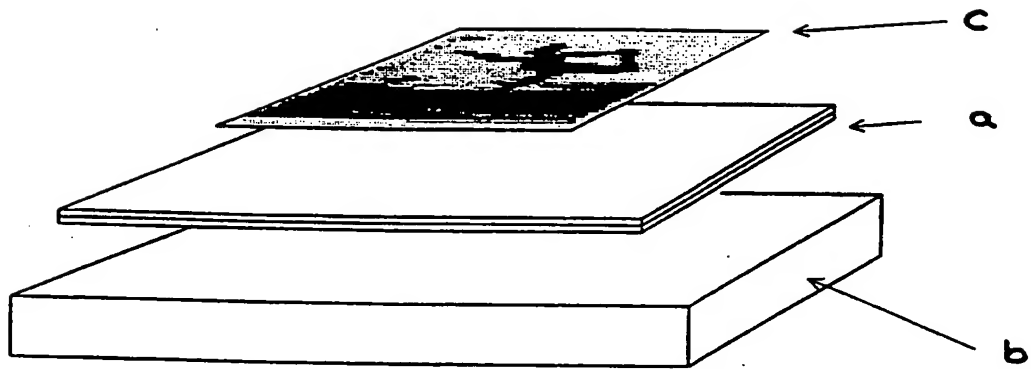
**Figure 3**



Figure 4.1

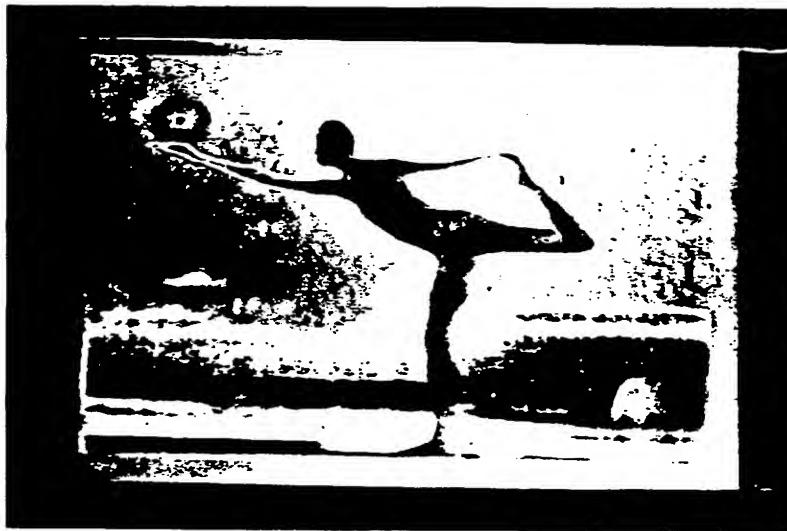


Figure 4.2

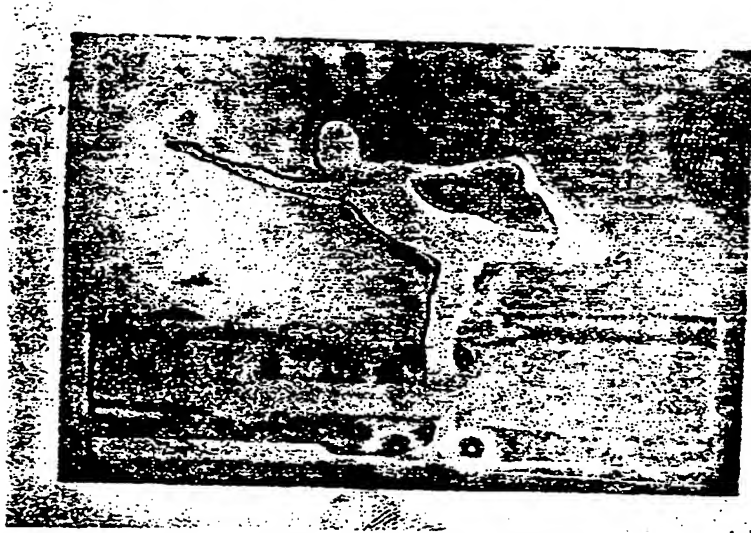


Figure 4.3

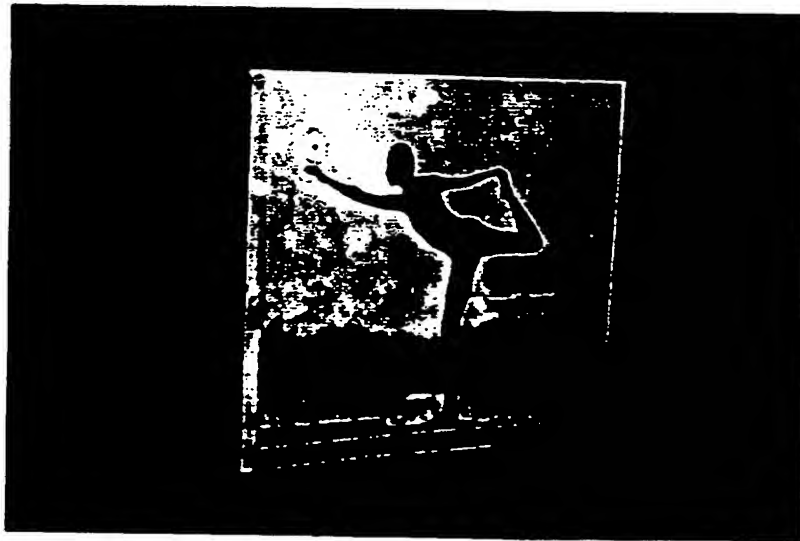


Figure 4.4

Thermochromic Polymerizable Mesogenic Composition

The invention relates to a thermochromic polymerizable mesogenic composition essentially consisting of

5

a) a component MA comprising at least one achiral polymerizable mesogenic compound comprising at least one polymerizable functional group,

10

b) a component MB comprising at least one chiral polymerizable mesogenic compound comprising at least one polymerizable functional group,

15

c) a photoinitiator, and

d) optionally a dye component.

20

25

The invention further relates to anisotropic polymers and polymer films with a chiral mesophase obtainable from said thermochromic polymerizable mesogenic composition and to the use of said thermochromic polymerizable mesogenic composition, of said anisotropic polymers and cholesteric polymer films for optical information storage, photomasks, decorative pigments, cosmetics, security applications, active and passive optical elements such as polarizers or optical retarders, colour filters, scattering displays, adhesives or synthetic resins with anisotropic mechanical properties.

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Figure 1.1 shows the change of the reflective colour versus the temperature of a thermochromic polymerizable mixture according to example 1 of the present invention.

35

Figure 1.2 shows the transmission spectra of polymer films obtained by curing a polymerizable thermochromic mixture according to example 1 of the present invention at different temperatures.

Figure 2 shows the change of the reflective colour versus the temperature of a thermochromic polymerizable mixture according to example 3 of the present invention.

5 Figure 3 shows the experimental setup for the preparation of a multi-colour image according to example 4 of the present invention.

10 Figure 4.1 shows a photomask used for the preparation of a multi-colour image according to example 4 of the present invention.

Figure 4.2 shows a multi-colour image according to example 4 of the present invention when being viewed against a dark background.

15 Figure 4.3 shows a multi-colour image according to example 4 of the present invention when being viewed in transmission.

20 Figure 4.4 shows a multi-colour image according to example 4 of the present invention when being viewed against a dark background at an oblique angle.

25 Thermochromic compositions, i.e. compositions that show a change of colour upon temperature variation, are known in prior art. Usually low molar mass liquid crystals exhibiting a chiral mesophase, like cholesteric liquid crystals (CLCs) are used in thermochromic compositions. These materials exhibit a helically twisted molecular structure and show selective reflection of a specific wavelength band of light, wherein the reflected wavelength maximum varies upon change of the temperature. Such thermochromic compositions are disclosed for example in the WO 90/02161.

30 For many applications, such as the preparation of coloured films that can be used as optical films like e.g. patterned colour filters, photomasks or films for optical information storage, materials like CLCs are needed wherein the reflected wavelength band remains
35 substantially constant over a wide temperature range.

5 A suitable material for these applications would be a polymerizable thermochromic composition, wherein the desired pitch length and thereby the waveband reflected from that composition could be easily selected by temperature variation and afterwards the molecular structure with the selected pitch be fixed by polymerization, so that the reflected wavelength remains stable over a wide temperature range.

10 The European Patent Application EP 0 661 287 A1 discloses polymerizable liquid crystalline siloxanes that show thermochromic behaviour and can be polymerized to give linear liquid crystalline polymers with mesogenic side chains.

15 However, linear polymers and in particular polymers comprising siloxane chains like those disclosed in EP 0 661 287 most often exhibit low glass transition temperatures and show only limited temperature stability. Upon heating of these polymers their optical properties are often deteriorating.

20 Consequently there has been a considerable demand for a thermochromic material that can be polymerized to give an anisotropic polymer or polymer film with a helical structure that exhibits a higher temperature stability and a reflection wavelength that remains substantially constant over a wide temperature range, and does not have the disadvantages of the materials of prior art as
25 discussed above.

One of the aims of the present invention is to provide a thermochromic polymerizable mesogenic composition having these properties.
30 Another aim of the invention is to provide an anisotropic polymer or polymer film that can be prepared by polymerization of such a composition. Yet another aim of the invention is a process of preparing a polymer film with a chiral mesophase from such a composition. Another aim of the present invention is to extend the pool of thermochromic polymerizable mesogenic materials available to the
35 expert. Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

It has been found that the above mentioned aims can be achieved by providing a thermochromic polymerizable mesogenic composition according to the present invention.

5

The terms polymerizable or reactive mesogen, polymerizable or reactive mesogenic compound or group or polymerizable or reactive liquid crystal or liquid crystalline compound as used in the foregoing and the following comprise compounds with a rod-shaped, board-shaped or disk-shaped mesogenic group. These compounds do not necessarily have to exhibit mesophase behaviour by themselves. In a preferred embodiment of the present invention they show mesophase behaviour in mixtures with other compounds or after polymerization of the pure mesogenic compounds or of the mixtures comprising the mesogenic compounds.

15

Preferably the polymerizable mesogenic compounds exhibit mesophase behaviour on their own.

20

The term "mesogeneity supporting group" as used in the foregoing and the following is indicating a rod-shaped, board-shaped or disk-shaped group, which does not necessarily have to show mesogenic behaviour (i.e. the ability to induce mesophase behaviour in a compound comprising such a group) alone. It is also possible that such a group shows mesogenic behaviour if being combined in a compound with other groups, or if the compound comprising the mesogeneity supporting group is polymerized or admixed with other compounds comprising the same or other mesogenic or mesogeneity supporting groups.

25

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One object of the present invention is a thermochromic polymerizable mesogenic composition essentially consisting of

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- a) a component MA comprising at least one achiral polymerizable mesogenic compound comprising at least one polymerizable functional group,

5 b) a component MB comprising at least one chiral polymerizable mesogenic compound comprising at least one polymerizable functional group,

c) a photoinitiator, and

d) optionally a dye component.

10 The components MA and MB comprise polymerizable mesogenic compounds with at least one polymerizable group. Preferably these polymerizable mesogenic compounds have up to four, in particular up to three, very preferably one or two polymerizable groups.

15 The achiral polymerizable compounds of component MA are preferably selected of formula I



20 in which

P is $CH_2=CH-COO-$, $WCH=CH-O-$, $WHC \begin{array}{c} \diagup O \diagdown \\ \text{---} \end{array} CH-$
or $CH_2=CH-Phenyl-(O)_k-$ with W being H, CH_3 or Cl and k being 0 or 1,

25

Sp is a spacer group having 1 to 20 C atoms,

30 X is a group selected from $-O-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-OCO-O-$, $-S-CO-$, $-CO-S-$ or a single bond,

n is 0 or 1,

35 MG is a mesogenic or mesogeneity supporting group preferably selected of formula II



wherein

5 Z^1 is in each case independently -COO-, -OCO-, -CH₂CH₂-,
-OCH₂-, -CH₂O-, -CH=CH-, -CH=CH-COO-, -OCO-CH=CH-,
-C≡C- or a single bond,

10 A^1 and A^2 are each independently 1,4-phenylene in which, in
addition, one or more CH groups may be replaced by N,
1,4-cyclohexylene in which, in addition, one or two non-
adjacent CH₂ groups may be replaced by O and/or S, 1,4-
cyclohexenylene, or naphthalene-2,6-diyl, it being possible
15 for all these groups to be unsubstituted, mono- or
polysubstituted with halogen, cyano or nitro groups or alkyl,
alkoxy or alkanoyl groups having 1 to 7 C atoms wherein
one or more H atoms may be substituted by F or Cl, and

20 m is 1, 2 or 3,
and

25 R is an achiral alkyl radical with up to 25 C atoms which may be
unsubstituted, mono- or polysubstituted by halogen or CN, it
being also possible for one or more non-adjacent CH₂ groups to
be replaced, in each case independently from one another, by -
O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-,
-CO-S- or -C≡C- in such a manner that oxygen atoms are not
30 linked directly to one another, or alternatively R is halogen, cyano
or has independently one of the meanings given for P-(Sp-X)_n-,

The chiral polymerizable compounds of component MB are preferably
selected of formula III



in which

P, Sp, X and n have the meanings given for formula I,

5 MG* is a mesogenic or mesogeneity supporting group, which is preferably selected of formula II given above, and

10 R* is H or an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S- or -C≡C- in such a manner that oxygen atoms are not
15 or has independently one of the meanings given for P-(Sp-X)_n.

wherein at least one of the groups MG* and R* is comprising at least one chiral structure element.

20 In a preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition comprises at least one polymerizable mesogenic compound comprising two or more polymerizable functional groups which is preferably selected of formula I or III.

25 Another object of the present invention is an anisotropic polymer with a chiral mesophase obtainable by polymerizing a thermochromic polymerizable mesogenic composition as described in the foregoing and the following.

30 Another object of the invention is an anisotropic polymer film with a chiral mesophase exhibiting a helically twisted molecular structure that is obtainable by

35 A) coating a thermochromic polymerizable mesogenic composition comprising

- 5
- a) a component MA comprising at least one achiral polymerizable mesogenic compound comprising at least one polymerizable functional group;
 - b) a component MB comprising at least one chiral polymerizable mesogenic compound comprising at least one polymerizable functional group,
 - c) a photoinitiator, and
 - d) optionally a dye component.
- 10

on a substrate or between two substrates in form of a layer,

- 15
- B) aligning the polymerizable mesogenic mixture so that the axis of the molecular helix extends transversely to the layer,
 - C) heating at least a part of the aligned mixture to a defined temperature,
 - D) polymerizing at least a part of the aligned mixture by exposure to actinic radiation,
 - E) optionally repeating step D) alone or together with step C) and /or steps A) and B) at least one more time, and
 - F) optionally removing the substrate or, if present, one or two of the substrates from the polymerized material.
- 20
- 25

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Yet another object of the present invention is a polymer film with a chiral mesophase obtainable by the process described above wherein at least one region of the film exhibits a pitch of the molecular helix that is different from at least one other region of the film.

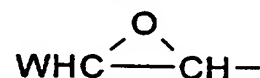
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Another object of the present invention is the use of a thermochromic polymerizable mesogenic composition, an anisotropic polymer or

polymer film with a chiral mesophase as described above and below for optical information storage, photomasks, decorative pigments, cosmetics, security applications, active and passive optical elements such as polarizers or optical retarders, colour filters, scattering displays, adhesives or synthetic resins with anisotropic mechanical properties.

The components MA and MB comprise polymerizable mesogenic compounds with at least one polymerizable group. Preferably these polymerizable mesogenic compounds have up to four, in particular up to three, very preferably one or two polymerizable groups.

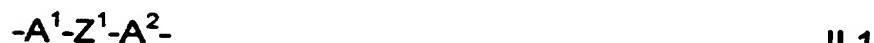
In the compounds of formula I and III P is denoting



$\text{CH}_2=\text{CW-COO}$, $\text{WCH}=\text{CH-O-}$ or $\text{CH}_2=\text{CH-Phenyl-(O)}_k\text{-}$ with W being H, CH_3 or Cl and k being 0 or 1.

Preferably P is a vinyl group, an acrylate or methacrylate group, a propenyl ether group or an epoxy group. Especially preferably P is an acrylate or methacrylate group.

MG in formula I and MG* in formula III are preferably selected of formula II. Formula II covers the bicyclic, tricyclic and tetracyclic mesogenic groups of the sub-formulae II 1 - II 3:



Bicyclic and tricyclic mesogenic groups of formula II are particularly preferred.

Of the mesogenic groups wherein A^1 and/or A^2 denote a heterocyclic group, those containing a pyridine-2,5-diyl group, pyrimidine-2,5-diyl group or 1,3-dioxane-2,5-diyl group are particularly preferred.

Of the preferred mesogenic groups containing a substituted 1,4-phenylene group very particularly preferred are those substituted by F, Cl or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms.

A smaller group of particularly preferred mesogenic groups of the formulae II 1, II 2 and II 3 is listed below. For reasons of simplicity, PheL is 1,4-phenylene, which is substituted in 2- and/or 3-position with L, wherein L denotes halogen, a cyano or nitro group or an alkyl, alkyloxy or alkanoyl group having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl. Furthermore, Pyd is pyridine-2,5-diyl, Pyr is pyrimidine-2,5-diyl, Cyc is 1,4-cyclohexylene, Cyh is 1,4-cyclohexenylene, Dio is trans-1,3-dioxane-2,5-diyl, Dit is trans-1,3-dithiane-2,5-diyl and Nap is a naphthalene-2,6-diyl group. The notations Pyd, Pyr, Dio and Dit in each case include the two possible positional isomers.

Z¹ in these groups, unless otherwise indicated, has the meaning given in formula I as described above and below.

Preferred two-ring mesogenic groups are those of formulae II 1-1 to II 1-27:

25	-Phe-Z ¹ -Phe-	II 1-1
	-Phe-Z ¹ -PheL-	II 1-2
	-PheL-Z ¹ -PheL-	II 1-3
	-Phe-Z ¹ -Cyc-	II 1-4
	-Cyc-Z ¹ -Phe-	II 1-5
30	-Cyc-Z ¹ -PheL-	II 1-6
	-Cyc-Z ¹ -Cyc-	II 1-7
	-Phe-Z ¹ -Pyd-	II 1-8
	-Phe-Z ¹ -Pyr-	II 1-9
	-PheL-Z ¹ -Pyd-	II 1-10
35	-PheL-Z ¹ -Pyr -	II 1-11
	-Pyd-Z ¹ -Pyr-	II 1-12

	-Pyd-Z ¹ -Pyd-	II 1-13
	-Phe-Z ¹ -Dio-	II 1-14
	-PheL-Z ¹ -Dio-	II 1-15
	-Phe-Z ¹ -Dit-	II 1-16
5	-PheL-Z ¹ -Dit-	II 1-17
	-Phe-Z ¹ -Cyh-	II 1-18
	-PheL-Z ¹ -Cyh-	II 1-19
	-Dio-Z ¹ -Dit-	II 1-20
	-Dio-Z ¹ -Dio-	II 1-21
10	-Phe-Z ¹ -Nap-	II 1-22
	-PheL-Z ¹ -Nap-	II 1-23
	-Nap-Z ¹ -Phe-	II 1-24
	-Nap-Z ¹ -PheL-	II 1-25
	-Nap-Z ¹ -Cyc-	II 1-26
15	-Pyd-Z ¹ -Nap-	II 1-27

In the formulae II 1-1 to II 1-27, Z¹ is preferably an ester group (-CO-O- or -O-CO-), -CH₂CH₂- or a single bond.

20 Of the mesogenic groups of formula II 1-1 to II 1-27, those of formula II 1-1 to II 1-13 are preferred. Especially preferred are the mesogenic groups of formula II 1-1 to II 1-7, in particular those of formula II 1-1 to II 1-4.

25 Preferred three-ring mesogenic groups are those of the formulae II 2-1 to II 2-23:

	-Phe-Z ¹ -Phe-Z ¹ -Phe-	II 2-1
	-PheL-Z ¹ -Phe-Z ¹ -Phe-	II 2-2
30	-Phe-Z ¹ -Phe-Z ¹ -PheL-	II 2-3
	-Phe-Z ¹ -PheL-Z ¹ -Phe-	II 2-4
	-PheL-Z ¹ -Phe-Z ¹ -PheL-	II 2-5
	-PheL-Z ¹ -PheL-Z ¹ -PheL-	II 2-6
	-Phe-Z ¹ -PheL-Z ¹ -PheL-	II 2-7
35	-PheL-Z ¹ -PheL-Z ¹ -Phe-	II 2-8
	-Phe-Z ¹ -Phe-Z ¹ -Cyc-	II 2-9

	-PheL-Z ¹ -Phe-Z ¹ -Cyc-	II 2-10
	-Phe-Z ¹ -Cyc-Z ¹ -Phe-	II 2-11
	-PheL-Z ¹ -Cyc-Z ¹ -Phe-	II 2-12
	-Cyc-Z ¹ -Cyc-Z ¹ -Phe-	II 2-13
5	-Cyc-Z ¹ -Phe-Z ¹ -Phe-	II 2-14
	-Phe-Z ¹ -Phe-Z ¹ -Cyc-	II 2-15
	-Phe-Z ¹ -Pyr-Z ¹ -Phe-	II 2-16
	-Phe-Z ¹ -Pyr-Z ¹ -Phe-	II 2-17
	-Phe-Z ¹ -Phe-Z ¹ -Pyr-	II 2-18
10	-Phe-Z ¹ -Phe-Z ¹ -Pyr-	II 2-19
	-Phe-Z ¹ -PheL-Z ¹ -Pyr-	II 2-20
	-Phe-Z ¹ -PheL-Z ¹ -Pyr-	II 2-21
	-Phe-Z ¹ -Pyr-Z ¹ -PheL-	II 2-22
	-Phe-Z ¹ -Pyr-Z ¹ -PheL-	II 2-23

15

Of the mesogenic groups of formula II 2-1 to 1-23, those of formula II 2-1 to II 2-15 are preferred. Especially preferred are the mesogenic groups of formula II 2-1 to II 2-10, in particular those of formula II 2-1 to II 2-4, II 2-9 and II 2-10.

20

In particular preferred are the compounds of formulae II 2-1 to II 2-23 in which Z¹ is independently from each other -COO-, -OCO- or a single bond.

25

Of these preferred compounds very particularly preferred are those of formula II 2-4, wherein PheL is especially preferably a 1,4-phenylene group substituted by an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms.

30

Preferred four-ring mesogenic groups are those of the formulae II 3-1 to II 3-12:

35

	-Phe-Z ¹ -Phe-Z ¹ -Phe-Z ¹ -Phe-	II 3-1
	-Phe-Z ¹ -Phe-Z ¹ -Phe-Z ¹ -PheL-	II 3-2
	-Phe-Z ¹ -Phe-Z ¹ -PheL-Z ¹ -Phe-	II 3-3
	-Phe-Z ¹ -PheL-Z ¹ -Phe-Z ¹ -Phe-	II 3-4

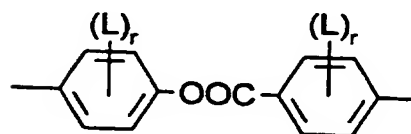
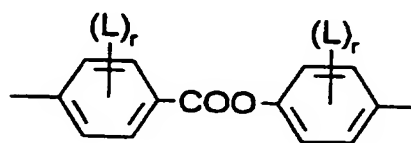
	-PheL-Z ¹ -Phe-Z ¹ -Phe-Z ¹ -Phe-	II 3-5
	-Phe-Z ¹ -PheL-Z ¹ -PheL-Z ¹ -Phe-	II 3-6
	-Phe-Z ¹ -Phe-Z ¹ -Phe-Z ¹ -Cyc-	II 3-7
	-Phe-Z ¹ -Cyc-Z ¹ -Phe-Z ¹ -Phe-	II 3-8
5	-Phe-Z ¹ -Cyc-Z ¹ -Phe-Z ¹ -Cyc-	II 3-9
	-Cyc-Z ¹ -Phe-Z ¹ -Phe-Z ¹ -Cyc-	II 3-10
	-Phe-Z ¹ -PheL-Z ¹ -Phe-Z ¹ -Cyc-	II 3-11
	-PheL-Z ¹ -PheL-Z ¹ -Phe-Z ¹ -Cyc-	II 3-12

10 Of the mesogenic groups of formula II 3-1 to II 3-12, those of formula II 3-1 to II 3-4, II 3-7 and II 3-10 are preferred. Especially preferred are the mesogenic groups of formula II 3-1 to II 3-4.

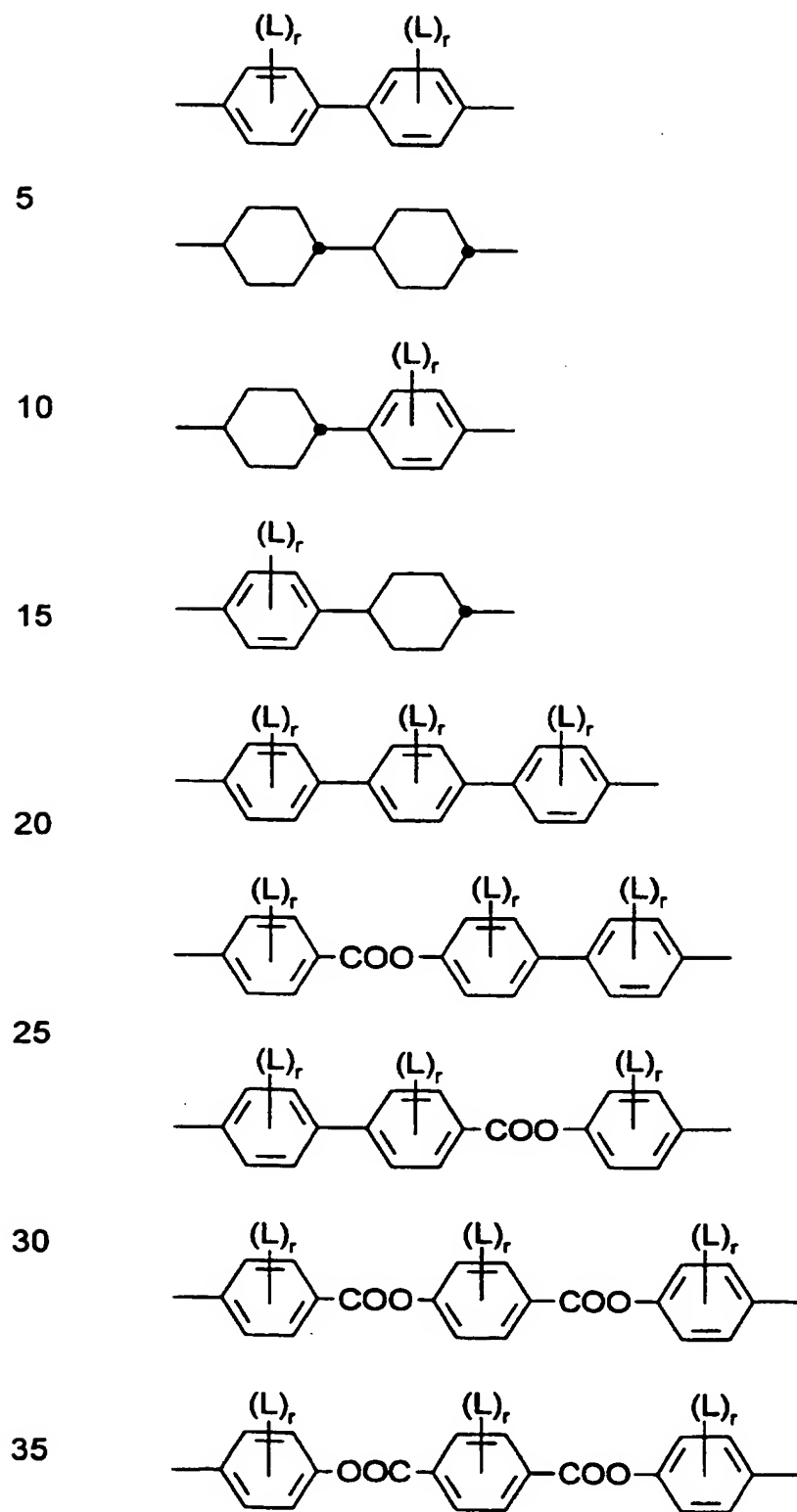
15 In the mesogenic groups of the formulae II 3-1 to II 3-12, at least one of the groups Z¹ is very particularly preferably a single bond.

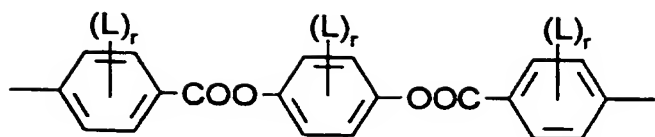
20 In the formulae I 1-1 to I 1-27, II 2-1 to II 2-23 and II 3-1 to II 3-12, L is preferably F, Cl, CN, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, CF₃, OCF₃, OCHF₂, OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ and OCF₃, most preferably F, CH₃, OCH₃ and COCH₃.

Particularly preferably MG and MG* are selected from the following formulae



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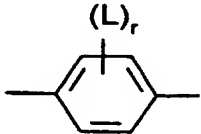
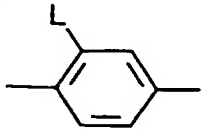
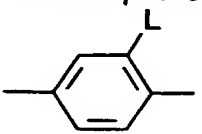
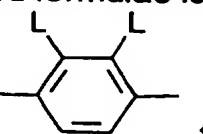




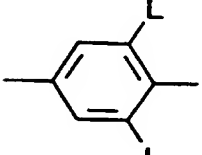
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wherein L has the meaning given above and r is 0, 1 or 2.

10

The group  in this preferred formulae is preferably denoting , ,  furthermore

15

, with L having each independently one of the meanings given above.

20

In the achiral polymerizable mesogenic compounds of the formula I, R is preferably an achiral alkyl radical which is unsubstituted or substituted by at least one halogen atom, it being possible for one or two non-adjacent CH₂ groups of these radicals to be replaced by -O-, -S-, O-CO-, -CO-O- or -O-CO-O- groups.

25

Halogen is preferably F or Cl.

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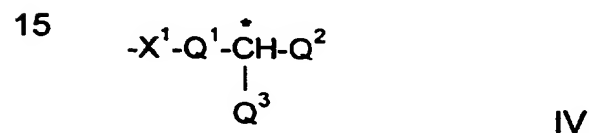
If R is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl,

35

tetradecyl, pentadecyl, methoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

5 Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

10 In the polymerizable mesogenic compounds of formula III R* may be an achiral or a chiral group. In case of a chiral group it is preferably selected according to the following formula IV:



20 wherein

X¹ has the meaning given for X,

25 Q¹ is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

30 Q² is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -C≡C-, -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO- or -CO-S- in such a manner that oxygen atoms are not linked directly to one another, or alternatively has the meaning given for P-Sp-,

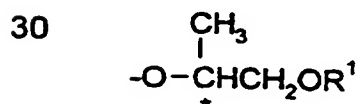
35 Q³ is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q².

Preferred chiral groups R* are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, for example.

In addition, mesogenic compounds of the formula I and/ or III containing an achiral branched group R or R* respectively may occasionally be of importance as comonomers, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropoxy and 3-methylbutoxy.

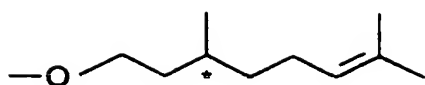
In another preferred embodiment R* in formula III is denoting a chiral group that is selected from the following groups:

an ethylenglycol derivative

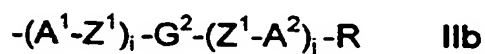


wherein R¹ is an alkyl radical with 1 to 12 C atoms,

or a group based on citronellol.



5 In another preferred embodiment of the present invention the compounds of formula III comprise a mesogenic or mesogenity supporting group MG^* having at least one center of chirality. In these compounds MG^* is preferably selected according to formula IIa or IIb:



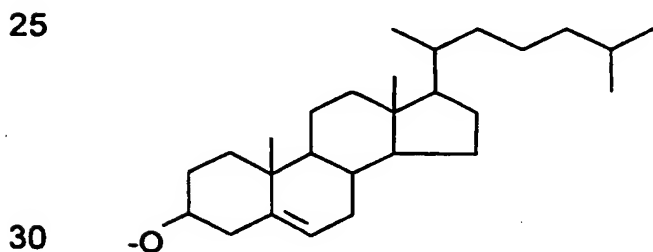
15 wherein

A^1 , A^2 and Z^1 have the meaning given in formula II,

R has the meaning given in formula I,

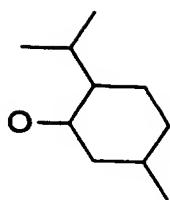
20 i and j are independently of each other 0, 1 or 2,

G^1 is a terminal chiral group, such as for example a cholesteryl group,



a terpenoid radical, for example as disclosed in the WO 96/17901, particularly preferably a menthyl group,

35



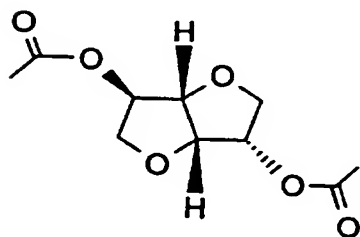
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a terminal chiral sugar or sugar-like group comprising a mono- or dicyclic radical with pyranose or furanose rings like, for example, a terminal group derived from the chiral sugar or sugar-like groups as disclosed in the WO 95/16007,

10

and G^2 is a bivalent chiral group, like for example a bivalent chiral sugar or sugar derivative or another bivalent chiral radical as disclosed e.g. in the WO 95/16007, especially preferably a group based on 1,4:3,6-Dianhydro-D-sorbitol:

15



20

In case G^2 is a group based on 1,4:3,6-Dianhydro-D-sorbitol as disclosed above, Z^1 is preferably denoting $-\text{CH}=\text{CH}-$.

25

As for the spacer group Sp all groups can be used that are known for this purpose to the skilled in the art. The spacer group Sp is preferably linked to the polymerizable group P by an ester or ether group or a single bond. The spacer group Sp is preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more, non-adjacent CH_2 groups may be replaced by $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{N}(\text{CH}_3)-$, $-\text{CO}-$, $-\text{O}-\text{CO}-$, $-\text{S}-\text{CO}-$, $-\text{O}-\text{COO}-$, $-\text{CO}-\text{S}-$, $-\text{CO}-\text{O}-$, $-\text{CH}(\text{halogen})-$, $-\text{CH}(\text{CN})-$, $-\text{CH}=\text{CH}-$ or $-\text{C}\equiv\text{C}-$.

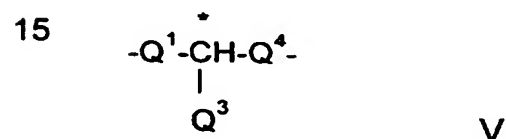
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Typical spacer groups Sp are for example $-(CH_2)_o-$, $-(CH_2CH_2O)_r-$, CH_2CH_2- , $-CH_2CH_2-S-CH_2CH_2-$ or $-CH_2CH_2-NH-CH_2CH_2-$, with o being an integer from 2 to 12 and r being an integer from 1 to 3.

5 Preferred spacer groups Sp are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene and 1-methylalkylene, for example.

10 In a preferred embodiment of the invention the polymerizable mesogenic compounds of formula III comprise a spacer group Sp that is a chiral group of the formula V:



20 wherein

Q^1 and Q^3 have the meanings given in formula IV, and

25 Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1 .

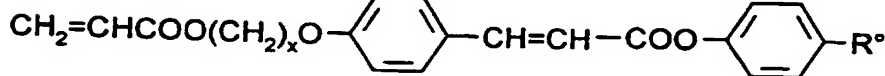
In particular preferred are compounds of formula I and/or III wherein n is 1.

30 In a preferred embodiment, the inventive anisotropic polymers and cholesteric polymer films are obtained by copolymerizing mixtures comprising compounds of formula I and /or formula III wherein n is 0 and compounds of formula I and/or formula III wherein n is 1.

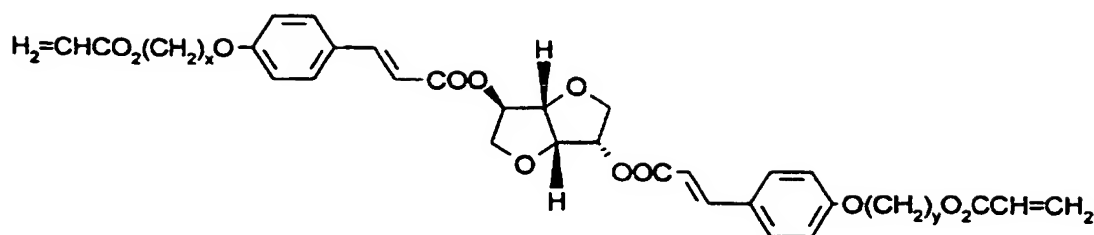
35 In the event that R, R^* or Q^2 is a group of formula P-Sp-X- or P-Sp- respectively, the spacer groups on each side of the mesogenic core may be identical or different.

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wherein x and y are each independently 1 to 12, D is a 1,4-phenylene or 1,4-cyclohexylene group, R^o is halogen, cyano or a chiral or achiral alkyl or alkoxy group with 1 to 12 C atoms and L¹ and L² are each independently H, Halogen, CN, or an alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms.

15

In a preferred embodiment of the present invention, the thermochromic polymerizable mesogenic composition comprises the following components

20

a1) 10 to 80 % by weight of component MA1 comprising at least one achiral polymerizable mesogenic compound according to formula I having one polymerizable functional group,

25

a2) 0 to 70 % by weight of component MA2 comprising at least one achiral polymerizable mesogenic compound according to formula I having two or more polymerizable functional groups,

30

b1) 10 to 95 % by weight of component MB1 comprising at least one chiral polymerizable mesogenic compound according to formula III having one polymerizable functional group,

b2) 0 to 30 % by weight of component MB2 comprising at least one chiral polymerizable mesogenic compound according to formula III having two or more polymerizable functional groups,

35

c) 0.01 to 5 % by weight of a photoinitiator, and

d) 0 to 20 % by weight of a dye component.

In a particularly preferred embodiment of the present invention, the thermochromic polymerizable mesogenic composition comprises

- 5 a1) 10 to 80 %, preferably 15 to 65 %, in particular 20 to 50 % by weight of two or more achiral polymerizable mesogenic compounds of component MA1,
- 10 a2) 1 to 70 %, preferably 2 to 55 %, in particular 4 to 40 % by weight of at least one achiral polymerizable mesogenic compound of component MA2,
- 15 b1) 10 to 95 %, preferably 15 to 90 %, in particular 20 to 80 % by weight of two or more chiral polymerizable mesogenic compounds of component MB1,

and further comprises component c) and optionally components b2) and d) in the concentration ranges as described above.

20 Compositions according to this particularly preferred embodiment are preferred that comprise two to eight, in particular two to six, most preferably two to four different compounds of component MA1 and two to eight, in particular two to six, most preferably two to four different compounds of component MB1 as described above.

25 The ratio of each of the compounds of component MA1 in the mixture according to this particularly preferred embodiment is preferably 5 to 75 %, in particular 8 to 65 %, very preferably 10 to 55 % by weight of the total mixture.

30 The ratio of each of the compounds of component MB1 in the mixture according to this particularly preferred embodiment is preferably 5 to 90 %, in particular 8 to 80 %, very preferably 10 to 70 % by weight of the total mixture.

35

Furthermore preferred are compositions according to this particularly preferred embodiment that comprise at least one compound of component MA2 in the concentration range as described above.

5 Further preferred are compositions according to the preferred embodiments described above that additionally comprise 0 to 30 %, preferably 0.1 to 20 %, in particular 0.5 to 15 % by weight of at least one non polymerizable chiral or chiral mesogenic compound, like e.g. a chiral dopant.

10 In the compositions comprising two or more different compounds of component MA1 and MB1 that are selected of formula I and III as described above, preferably each of the different compounds according to formula I and III is different in at least one of the groups
15 P, Sp, X, MG, MG*, R or R* from each other of the compounds of the same component.

In another preferred embodiment of the present invention the thermochromic polymerizable compositions contain less than 10 %
20 by weight, very especially preferably none of the compounds of component MA2 and MB2.

Another object of the present invention are anisotropic polymers with a chiral mesophase that can be prepared by polymerization of an
25 inventive thermochromic polymerizable mesogenic composition according to the present invention. Polymerization can be carried out as polymerization in solution or as in-situ polymerization.

30 Preferably the anisotropic polymers are prepared as thin films by in-situ polymerization of inventive thermochromic polymerizable mesogenic compositions.

For this purpose, an inventive polymerizable composition is coated
35 onto one substrate or between two substrates and aligned, which can easily be achieved by conventional techniques. The alignment is subsequently frozen in by curing of the composition to give

anisotropic polymer films with uniform orientation. Curing can be achieved by exposure of the inventive thermochromic polymerizable mesogenic compositions to actinic radiation in the presence of an initiator absorbing at the wavelength of said radiation.

5

A detailed description of this method can be found in D.J.Broer et al., Makromol.Chem. **190**, pp. 2255 ff. (1989).

10

As a substrate for example a glass or quartz sheet as well as a plastic film or sheet can be used. It is also possible to put a second substrate on top of the coated mixture prior to, during and/or after polymerization. The substrates can be removed after polymerization or not. When using two substrates in case of curing by actinic radiation, at least one substrate has to be transmissive for the actinic radiation used for the polymerization.

15

Isotropic or birefringent substrates can be used. In case the substrate is not removed from the polymerized film after polymerization, preferably isotropic substrates are used.

20

It is also possible to use plastic films as substrates, for example plastic films that can be used in film production, like e.g. polyester films such as polyethyleneterephthalate (PET), or films of polyvinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC). As a birefringent substrate for example an uniaxially stretched plastic film can be used. Preferably at least one substrate is a plastic substrate, especially preferably a PET film or a TAC film. PET films are commercially available e.g. from ICI Corp. under the trade name Melinex.

25

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The coated layer of the inventive mixture of the polymerizable mesogenic material is preferably aligned to give a planar orientation, i.e. an orientation so that the axis of the molecular helix extends transversely to the layer.

35

A planar orientation can be achieved for example by shearing the material, e.g. by means of a doctor blade. It is also possible to apply an alignment layer, for example a layer of rubbed polyimide or sputtered SiO_x , on top of at least one of the substrates.

5

In another preferred embodiment, a second substrate is put on top of the coated material. In this case, the shearing caused by putting together the two substrates is sufficient to give good alignment.

10

Polymerization of the inventive polymerizable mesogenic mixture takes place by exposing it to actinic radiation in the presence of an initiator absorbing at the wavelength of said radiation.

15

Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

20

For example, when polymerizing by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerization reaction.

25

It is also possible to use a cationic photoinitiator, when curing reactive mesogens with for example vinyl and epoxide reactive groups, that photocures with cations instead of free radicals

30

As a photoinitiator for radical polymerization for example the commercially available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerization the commercially available UVI 6974 (Union Carbide) can be used.

35

In some cases it is of advantage to apply a second substrate not only to aid alignment of the polymerizable composition but also to exclude

oxygen that may inhibit the polymerization. Alternatively the curing can be carried out under an atmosphere of inert gas. However, curing in air is also possible using suitable photoinitiators and high lamp power. When using a cationic photoinitiator oxygen exclusion most often is not needed, but water should be excluded.

In a preferred embodiment of the invention the polymerization of the polymerizable mesogenic material is carried out under an atmosphere of inert gas, preferably under a nitrogen atmosphere.

In addition to light sensitive initiators the thermochromic polymerizable mesogenic composition according to the present invention may also comprise one or more other suitable components such as, for example, catalysts, stabilizers, chain-transfer agents, co-reacting monomers or surface-active compounds.

In a preferred embodiment of the invention, the thermochromic polymerizable mesogenic composition comprises a stabilizer that is used to prevent undesired spontaneous polymerization for example during storage of the composition. As stabilizers in principle all compounds can be used that are known to the skilled in the art for this purpose. These compounds are commercially available in a broad variety. Typical examples for stabilizers are 4-ethoxyphenol or butylated hydroxytoluene (BHT).

It is also possible, in order to increase crosslinking of the polymers, to add up to 20% of a non mesogenic compound with two or more polymerizable functional groups to the polymerizable composition alternatively or additionally to the multifunctional polymerizable mesogenic compounds.

Typical examples for difunctional non mesogenic monomers are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples for non mesogenic monomers with more than two polymerizable groups are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

5 Polymerization of inventive compositions comprising compounds with only one polymerizable functional group leads to linear polymers, whereas in the presence of compounds with more than one polymerizable functional group crosslinked polymers are obtained.

10 By varying the concentration of the multifunctional mesogenic or non mesogenic compounds the crosslink density of the polymers and thereby their physical and chemical properties such as the glass transition temperature, thermal and mechanical stability or the solvent resistance can be tuned easily.

15 In particular polymer films comprising crosslinked polymers show very high thermal stability of the optical and mechanical properties, depending on the degree of crosslinking, when compared to linear polymers. For example when an inventive thermochromic composition comprising a polymerizable mesogenic compound having two polymerizable groups is polymerized, the helical
20 structure of the chiral mesophase of the composition upon polymerization is fixed and a polymer film is obtained that shows a helical pitch that is remaining substantially constant upon temperature variation.

25 In a preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition comprises at least one compound of component MA selected of formula I having at least two polymerizable mesogenic groups and/or at least one
30 compound of component MB selected of formula III having at least two polymerizable mesogenic groups. Such a composition upon polymerization gives crosslinked polymers.

35 The inventive polymerizable mesogenic compositions are characterized in that they show thermochromic behaviour. This behaviour is shown by compositions or compounds that exhibit a chiral liquid crystalline phase or chiral mesophase, like e.g. a chiral

5 smectic phase or a chiral nematic (= cholesteric) phase, with a helically twisted molecular structure that shows selective reflection of a specific waveband of light, wherein the pitch of the molecular helix and thereby the reflected wavelengths are depending on the temperature.

10 Especially preferred are inventive thermochromic compositions that exhibit a cholesteric phase. Of these preferred compositions, further preferred are compositions that exhibit a cholesteric phase and a smectic phase, most preferably a chiral smectic phase, at temperatures below the temperature range of the cholesteric phase.

15 The inventive thermochromic compositions can show positive temperature dependency of the pitch, which means that the pitch increases with increasing temperature, or alternatively they can exhibit negative temperature dependency, which means that the pitch decreases with increasing temperature.

20 Thus, upon heating or cooling of an inventive thermochromic composition in its chiral mesophase a shift of the reflection maximum of the wavelengths reflected by the composition to higher or lower values is observed.

25 In a preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition exhibits a chiral mesophase with negative temperature dependency of the pitch, i.e. the pitch decreases with increasing temperature.

30 In another preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition exhibits a chiral mesophase with positive temperature dependency of the pitch, i.e. the pitch increases with increasing temperature.

35 In case the reflection maximum of the composition is in the visible range of light, a colour change of the inventive thermochromic

composition upon heating or cooling within its chiral mesophase is observed.

5 The above mentioned colour changes can be observed not only for the reflective colours of the composition, but also for the complementary secondary colours of the composition when being viewed in transmission (e.g. against a light source), e.g. if the inventive thermochromic composition is coated as a thin film onto a transparent substrate.

10 The pitch length and the thermochromic behaviour of the inventive thermochromic polymerizable compositions can be influenced by the ratio of the achiral compounds to the chiral compounds in the composition. With increasing ratio of the chiral compounds usually
15 the pitch length of the composition as well as the pitch length of the polymers and polymer films obtainable from this composition is decreasing.

20 It is also possible to add, for example, a quantity of up to 20% by weight of a non polymerizable liquid-crystalline compound to adapt the optical properties of the the polymers and polymer films obtainable from these compositions.

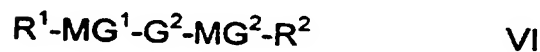
25 In some cases it is useful to add one or more non polymerizable chiral compounds, preferably non polymerizable chiral mesogenic compounds, to the inventive thermochromic composition to influence the pitch length and the thermochromic behaviour of the composition and of the polymers and polymer films obtainable from this
30 composition.

35 In a preferred embodiment of the present invention the inventive thermochromic composition additionally comprises 0 to 30 %, preferably 0 to 20 %, in particular 0.1 to 20%, very preferably 0.5 to 15 % by weight of at least one non polymerizable chiral or chiral mesogenic compound.

5 As a non polymerizable chiral mesogenic compound in principal all compounds can be used that are known to the skilled in the art for this purpose. Typical compounds are e.g. the commercially available chiral dopants S 1011, R 811 or CB 15 (Merck KGaA, Darmstadt, Germany).

10 As non polymerizable chiral mesogenic compounds preferably one or more chiral dopants are added to the inventive composition that comprise a chiral group MG^* and/or R^* as given in formula III.

Further preferred chiral dopants are selected of formula VI



15 wherein MG^1 and MG^2 each independently have one of the meanings of MG in formula II, R^1 and R^2 are each independently halogen, cyano or an optionally halogenated alkyl, alkoxy or alkanoyl group with 1 to 12 C atoms, and G^2 has the meaning of formula IIb. Very preferably G^2 is a chiral bivalent structure element based on a sugar molecule.

20 Upon polymerization, the cholesteric structure and the reflection maximum of an inventive composition can be fixed, as described above. When an inventive thermochromic composition is polymerized in the cholesteric phase at different temperatures, 25 polymer films are obtained that exhibit different reflection maxima of the wavelengths reflected by the films. If the different reflection maxima of the polymer films are in the visible wavelength range, films of different colour are obtained.

30 Alternatively it is possible to polymerize different parts of the same thermochromic composition at different temperatures and thereby to obtain a polymer film exhibiting different parts with different reflective colours.

35 Thus, by polymerization of an inventive thermochromic polymerizable composition, it is possible to prepare a polymer film wherein the

reflection maximum and thus the reflective colour that can be tuned easily by varying the polymerization temperature and/or the ratio of the chiral and achiral components of the composition.

- 5 Another object of the present invention is a process to prepare an anisotropic polymer film with a chiral mesophase from the inventive thermochromic polymerizable mesogenic composition. This process preferably implies the following steps
- 10 A) coating a thermochromic polymerizable mesogenic composition as described above and below on a substrate or between two substrates in form of a layer,
- 15 B) aligning the polymerizable mesogenic composition so that the axis of the molecular helix extends transversely to the layer,
- C) heating at least a part of the aligned composition to a defined temperature,
- 20 D) polymerizing at least a part of the aligned composition by exposure to actinic radiation,
- E) optionally repeating step D) alone or together with step C) and /or steps A) and B) at least one more time, and
- 25 F) optionally removing the substrate or, if present, one or two of the substrates from the polymerized material.

30 A preferred embodiment of the present invention relates to a process as described above, wherein the coated and aligned layer of the inventive thermochromic polymerizable mesogenic composition is heated in step C) to a defined temperature within the chiral mesophase of the composition, and wherein during subsequent polymerization in step D) a part of the layer is covered with a photomask that is not transmissive for the actinic radiation used for

35 polymerization. Thereby only the unmasked portions of the layer are

polymerized and the helical pitch and the reflection maximum in these unmasked portions of the layer are fixed.

5 The photomask is then removed, the layer is heated or cooled to a temperature that is different from that of the previous step C) and the parts of the layer that remained unmasked during the previous step D) are polymerized.

10 The steps C) and D) of the process according to this preferred embodiment can be repeated at least one more time, wherein the layer in each repeated step C) is heated or cooled to a temperature that is different from the previous step C), and in each repeated step D) a part of the layer is masked during polymerization that is different from the part of the layer that was masked in the previous step D).

15 Particularly preferred is a process according to this preferred embodiment wherein step C) and D) are repeated at least two times.

20 According to this preferred embodiment a polymer film exhibiting a chiral mesophase with a pattern of the helical pitch is obtained, i.e. a polymer film in which at least one of the different parts that have been masked during one of the polymerization steps D) exhibits a reflection maximum that is different from the reflection maxima of at least one of the parts that have been masked during the other
25 polymerization steps D) and/or from the unmasked parts.

Another preferred embodiment of the present invention is related to a process for preparing a polymer film as described above, in which as
30 a substrate in step A) another polymer film is used that was prepared in analogy to the process comprising steps A) to F) described above.

Thus it is possible to prepare a multilayer of polymer films with a chiral mesophase with a pattern of the helical pitch, i.e. a multilayer of films wherein each of the layers comprises at least one region with
35 a reflection maximum that is different from at least one other region of the same layer and/or of least one other layer.

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5 In another preferred embodiment of the present invention a photomask is used that comprises different parts having different transmissivity for the actinic radiation used for polymerization. As such a photomask it is possible to use e.g. a black and white photocopy or photograph that is printed or copied on a transparent material and exhibits different grey shades.

10 Preferably the photomask exhibits at least two, very preferably at least 5, in particular at least 10 different parts having different transmission of the actinic radiation used for polymerization of the inventive thermochromic polymerizable composition.

15 The photomask is put on the inventive thermochromic polymerizable mesogenic composition prior to polymerization, and the composition is irradiated at a given temperature with a burst of actinic radiation that is short enough so that only the parts of the polymerizable composition beneath the most transparent parts of the photomask are polymerized, freezing in the reflection colour at this temperature,
20 whereas the other parts of the composition remain unpolymerized.

The mixture is then heated or cooled, whereby the unpolymerized parts of the thermochromic mixture undergo a change of the reflection maximum and the reflective colour, and the mixture is
25 exposed to another burst of actinic radiation, so that the parts of the mixture beneath the less transparent parts of the photomask are polymerized and their colour is freezed in.

30 If the process comprising the above described heating/cooling and polymerization steps is repeated several times a multi-colour image can be obtained. The number of different colours and the colour shades of such a multi-colour image can be controlled by adjusting the process parameters, such as the intensity of the actinic radiation used in each polymerization step, the total time of exposure of the
35 polymerizable composition to the actinic radiation, the exposure time for each polymerization step, the number and intensity of the grey

scales of the photomask, the polymerization temperature at each step, and the total number of the heating and polymerization steps.

5 Another preferred embodiment of the present invention relates to a process comprising steps A) to F) described above, wherein in step D) one or more selected parts of the layer are polymerized by exposure to actinic radiation that is emitted by a finely focussed irradiation source like, for example, a laser beam.

10 The polymerizable composition according to this preferred embodiment should preferably comprise a photoinitiator that shows absorption of the emission wavelength of the laser used for polymerization.

15 Another particularly preferred embodiment of the present invention relates to a process comprising steps A) to F) described above, wherein in step C) one or more selected parts of the coated and aligned layer of the inventive thermochromic composition are heated to a defined temperature by exposure to a finely focussed irradiation
20 source like, for example, a laser beam.

The parts of the layer that are selectively heated in step C) by a laser beam according to this particularly preferred embodiment are very preferably polymerized in step D) by exposure to a second laser
25 beam that immediately traces the path of the first laser beam that was used in step C).

For example, for this particularly preferred embodiment an inventive composition can be used that comprises an IR dye and a photoinitiator
30 absorbing visible light, like e.g. Irgacure 1700 (Ciba Geigy AG). The heating of a selected part of the coated composition is carried out with an IR laser, and polymerization of the heated parts is achieved with a visible laser following the IR laser.

35 Further preferred is a process according to this particularly preferred embodiment wherein the heating of one or more selected parts of the

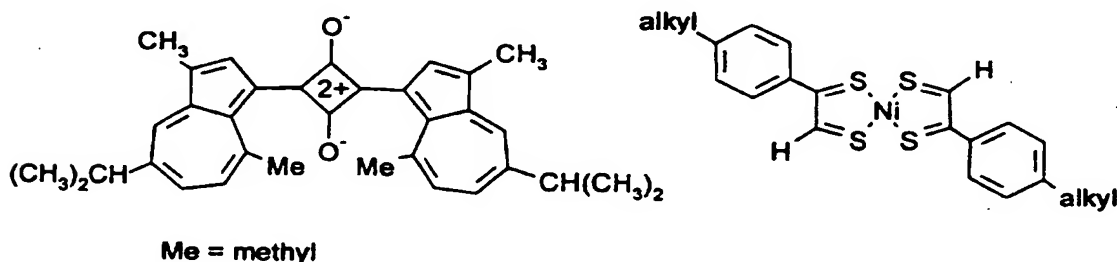
layer and the polymerization of these selectively heated parts of the layer are achieved by irradiation with the same laser.

5 In order to effectively absorb the irradiation of the laser that is used for heating selected parts of the layer according to the preferred embodiments described above, the thermochromic polymerizable mesogenic composition preferably comprises a dye component that comprises one or more dye compounds and is absorbing at the emission wavelength of the laser that is used for heating selected parts of the layer in step C) of the above described process.

15 As a suitable dye for example an IR dye, a UV dye or a dye absorbing in the visible wavelength range can be used. A dichroic dye can also be used. The dye component should be adjusted to exhibit absorption in the range of the wavelength emitted from the laser.

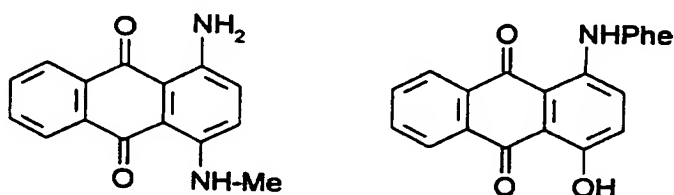
20 Suitable dye compounds are described in the literature and can be chosen, for example from the group of benzophenones, benzotriazoles, cinnamic and salicylic acids and their respective derivatives, anthraquinone and azo or azoxy dyes, organic Ni complex compounds, natural substances such as, for example, umbelliferon and yellow dyes like, for example, methyl yellow.

25 In a particularly preferred embodiment of the present invention the thermochromic polymerizable mesogenic composition comprises a dye component that comprises one or more dye compounds that are absorbing in the IR wavelength range, like e.g. the commercially available SC100870 (ICI Corp.) or like e.g. the following compounds



In another preferred embodiment of the invention a dye component is used that comprises one or more dye compounds that show absorption of He-Ne light (633 nm), like e.g. the following compounds

5

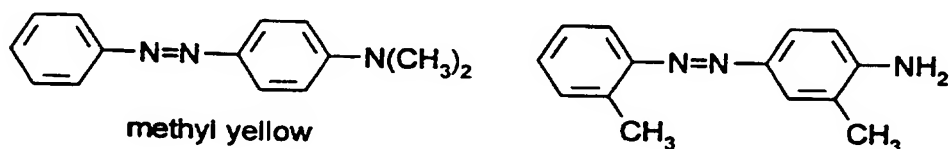


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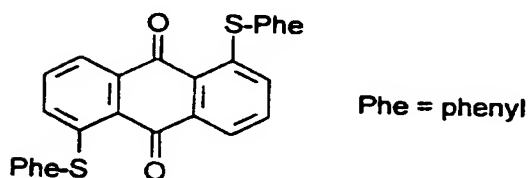
Me = methyl Phe = phenyl

In another preferred embodiment of the invention a dye component is used that comprises one or more dye compounds showing absorption of UV light, like e.g. the following dye compounds

15



20



25

It is also possible to use a semiconductor laser with an emission wavelength in the range between 750 and 950 nm and a dye component adjusted to significantly absorb in this wavelength range.

30

The examples of dye compounds given above should be taken only as illustrative and are in no way intended to restrict, but instead to explain the present invention.

35

In another preferred embodiment of the invention the thermochromic polymerizable mesogenic composition preferably comprises a dye component comprising one or more dye compounds that are absorbing at the emission wavelength of the laser that is used for

polymerization in step D) of the above described process. This dye component can effectively absorb the irradiation of the laser that is used for polymerization in order to reduce the curing time and/or to increase the polymerization rate.

5

This dye component is preferably chosen to be adjusted to exhibit a significant absorption in the range of the wavelength emitted from the laser that is used for polymerization in step D) as described above. In principal all the types and examples of dye compounds mentioned above can be used for this purpose.

10

In another preferred embodiment a photoinitiator is used in order to both absorb the emission wavelength of the laser used for heating the polymerizable composition and start the polymerization reaction.

15

If the inventive compositions comprise a dye component described above and below, the ratio of the dye component is preferably 0.1 to 20 %, very preferably 0.5 to 10 %, in particular 1 to 5 % by weight of the total mixture.

20

The dye component is preferably comprising one to six, very preferably one to three, in particular one or two dye compounds. Most preferably a single dye compound is used.

25

A polymerized film obtainable from an inventive thermochromic polymerizable mesogenic composition by a process according to one of the preferred embodiments or according to one of the examples as described above and below exhibits special colour properties.

30

For example, the film exhibits one or more reflection colours, which can be seen particularly well when being viewed against a dark background, and also shows the corresponding complementary colours when being viewed in transmission.

35

Furthermore, when being viewed against a dark background, such a film exhibits a colour shift to shorter wavelengths.

Due to these special properties, which are very difficult to reproduce by other than the above described inventive methods, the inventive polymerized films are particularly suitable for security applications, such as false-proof identity or credit cards, banknotes, watermarks etc..

In particular a multi-colour image prepared by a multi-step curing process and by using a photomask exhibiting various grey shades, as described in the above preferred embodiment, is suitable for a use in security applications.

Without further elaboration one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight. The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds:

K = crystalline; N = nematic; S = smectic; Ch = cholesteric; I = isotropic. The numbers between these symbols indicate the phase transition temperatures in degree Celsius.

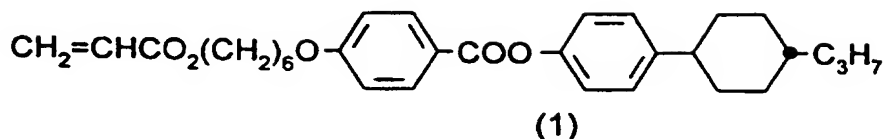
Example 1

The following polymerizable mixture is formulated

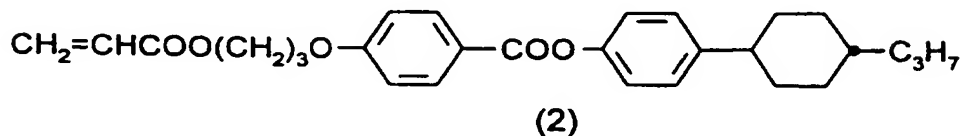
compound (1)	16.5 %
compound (2)	11.0 %
compound (3)	55.0 %
compound (4)	12.0 %

compound (5) 5.0 %
Irgacure 651 0.5 %

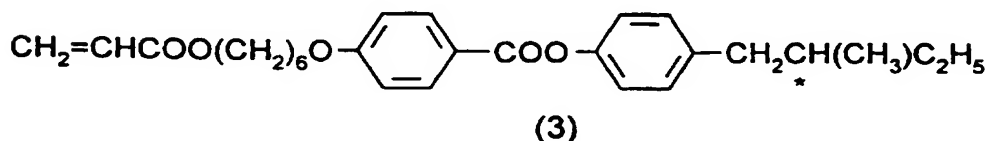
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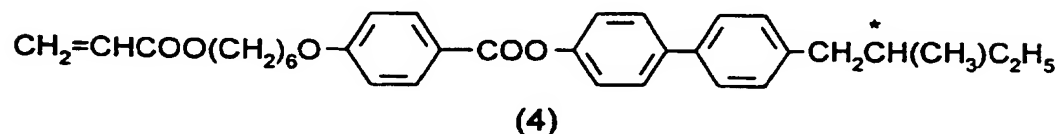
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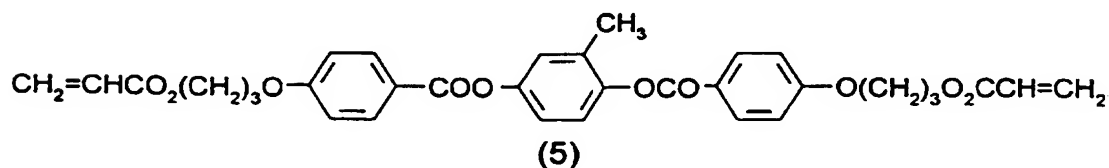
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20



25



30

The compounds (1) and (2) are prepared in analogy to the methods described in WO 93/22397 and DE 195,04,224.

Irgacure is a photoinitiator commercially available from Ciba Geigy AG (Basel, Switzerland).

The mixture shows the liquid crystal phase behaviour S 26.7 Ch 67.2 I.

35

The mixture exhibits the following colour appearance when heated from the smectic phase (the numbers are temperature values in °C):

Smectic 26.7 Cholesteric Phase, Red 29 Light Green 31 Bright Green
41 Light Blue 50 Deep Blue 59 Violet Blue 67.2 Isotropic Phase.

5 The central wavelength of the reflective colour shown by a thin film of this mixture at different temperatures was measured and is shown in Figure 1.1.

10 Polymer films of different colour are prepared by filling samples of the mixture between two glass plates and curing by exposure to UV radiation at different temperatures.

The colours of 3 polymer films prepared at different temperatures as described above are shown in the following table.

15

Film No.	Curing Temperature (°C)	Colour
1a	27	red
1b	33	green
1c	50	blue

20

Figure 1.2 shows the transmission spectra of the film samples 1a, 1b and 1c obtained as described above.

Example 2

25

The following mixture is formulated

compound (1) 15.0 %

compound (2) 9.5 %

compound (3) 45.0 %

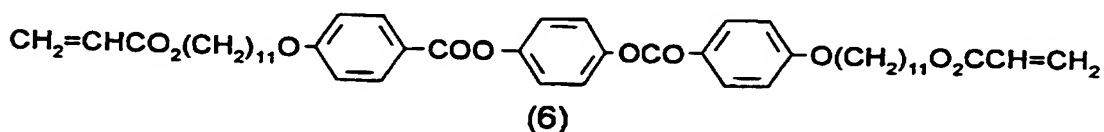
30

compound (4) 20.0 %

compound (6) 10.0 %

Irgacure 651 0.5 %

35



The compound (6) is prepared in analogy to the methods described in WO 93/22397 and DE 195,04,224.

5 The mixture shows the liquid crystal phase behaviour S 30.3 Ch 80.8 I.

The mixture exhibits the following colour appearance when heated from the smectic phase (the numbers are temperature values in °C):

10 Smectic Phase 30.3 Cholesteric Phase, Red 29 Light Green 31
Bright Green 41 Light Blue 50 Deep Blue 59 Violet Blue 67.2
Isotropic Phase

15 Polymer films of different colour are prepared by filling samples of the mixture between two glass plates and curing by exposure to UV radiation at different temperatures.

20 The colours of 3 polymer films prepared at different temperatures as described above are shown in the following table.

Film No.	Curing Temperature (°C)	Colour
2a	38	red
2b	46	green
2c	76	blue

25

Example 3

The following mixture is formulated

30 compound (1) 18.0 %
compound (2) 12.0 %
compound (3) 50.5 %
compound (4) 13.5 %
compound (5) 5.0 %
Irgacure 369 1.0 %

35

Irgacure 369 is a photoinitiator available from Ciba Geigy AG.

The mixture shows the liquid crystalline phase behaviour S 24 Ch 65 I.

5 The colour appearance of the mixture in the cholesteric phase when heated from the smectic phase is depicted in figure 2.

The mixture can be cured by UV irradiation as described in examples 1 and 2 at different temperatures selected from the curve in figure 2 to give polymer films of different colours.

10

Example 4

15 A thin film of the polymerizable mixture of example 1 with a thickness of 5 μm is prepared between two polyester substrates (Melinex 401, 100 μm). As illustrated by Figure 3, the sample (3a) comprising the film and the substrates is placed onto a temperature controlled plate (3b) at 22 °C to give a red reflection colour when viewed at normal incidence. A black and white photocopy onto a clear acetate film (standard foil used for overhead projection) is prepared from a photograph as shown in Figure 4.1 and placed as a photomask (3c) directly onto the sample as depicted in Figure 3.

20

25 The sample comprising the film of the polymerizable mixture and the mask are irradiated for 2 seconds with UV light from a metal halide source (irradiance 50 mW/cm^2), which causes the areas of the film of the polymerizable mixture beneath the most transparent parts of the photomask to polymerize and thus freezes in the red reflection colour in these areas.

30 The temperature of the hot plate is increased to 23 °C, which leads to a orange/yellow colour shift in the unpolymerized parts of the mixture. The system of the sample and the photomask is again irradiated with a short burst of UV light as described above, which causes the parts of the polymerizable mixture beneath the less transparent areas of the photomask to polymerize and thus freezes in the new colour.

35

5 This process of increasing the temperature of the hot plate to give a different reflective colour and then irradiating with a short burst of UV light is repeated at 25 °C, 30 °C and 35 °C. The mask is then removed and a final burst of UV irradiation is given at 40 °C to polymerize any areas of the sample which have not fully polymerized up to that point.

10 In this way a multi-colour image as shown in Figure 4.2 is produced with the colour at any given area being determined by the relative opacity of the mask to UV light.

15 When the sample is held against a bright background, the complementary colours of the reflection colours of the different parts of the sample are revealed as shown by Figure 4.3.

20 When being viewed at against a dark background at oblique angles, the sample shows a colour shift to shorter wavelengths, as shown by Figure 4.4.

25 Both the feature of complementary colours when viewed in transmission as depicted in Figure 4.3 and the colour shift to shorter wavelengths when viewed at oblique angles as depicted in Figure 4.4 are very difficult to reproduce by other methods. Thus a multi-colour image prepared as described above is well suitable in security applications, such as e.g. false-proof identity cards, credit cards, banknotes, watermarks etc..

30 The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

35 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various

changes and modifications of the invention to adapt it to various usages and conditions.

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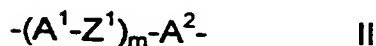
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Patent Claims

1. A thermochromic polymerizable mesogenic composition essentially consisting of
- 5
- a) a component MA comprising at least one achiral polymerizable mesogenic compound comprising at least one polymerizable functional group,
- 10
- b) a component MB comprising at least one chiral polymerizable mesogenic compound comprising at least one polymerizable functional group,
- 15
- c) a photoinitiator, and
- d) optionally a dye component.
2. A thermochromic polymerizable mesogenic composition according to claim 1, characterized in that the achiral polymerizable compounds of component MA are selected of formula I
- 20
- $$P-(Sp-X)_n-MG-R \quad I$$
- 25
- in which
- P is $CH_2=CW-COO-$, $WCH=CH-O-$, $WHC \begin{array}{c} \diagup O \diagdown \\ \text{---} \end{array} CH-$ or $CH_2=CH-Phenyl-(O)_k-$ with W being H, CH_3 or Cl and k being 0 or 1,
- 30
- Sp is a spacer group having 1 to 20 C atoms,
- X is a group selected from $-O-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-OCO-O-$, $-S-CO-$, $-CO-S-$ or a single bond,
- 35
- n is 0 or 1,

MG is a mesogenic or mesogenity supporting group of formula II



5 wherein

10 Z^1 is in each case independently -COO-, -OCO-,
-CH₂CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -CH=CH-COO-,
-OCO-CH=CH-, -C≡C- or a single bond,

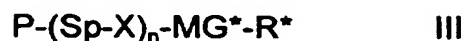
15 A^1 and A^2 are each independently 1,4-phenylene in which,
in addition, one or more CH groups may be replaced
by N, 1,4-cyclohexylene in which, in addition, one or
two non-adjacent CH₂ groups may be replaced by O
and/or S, 1,4-cyclohexenylene, or naphthalene-2,6-
diyl, it being possible for all these groups to be
unsubstituted, mono- or polysubstituted with halogen,
cyano or nitro groups or alkyl, alkoxy or alkanoyl
20 groups having 1 to 7 C atoms wherein one or more H
atoms may be substituted by F or Cl, and

m is 0, 1, 2 or 3, and

25 R is an achiral alkyl radical with up to 25 C atoms which may
be unsubstituted, mono- or polysubstituted by halogen or
CN, it being also possible for one or more non-adjacent CH₂
groups to be replaced, in each case independently from one
another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-,
30 -OCO-, -OCO-O-, -S-CO-, -CO-S- or -C≡C- in such a
manner that oxygen atoms are not linked directly to one
another, or alternatively R is halogen, cyano or has
independently one of the meanings given for $P-(Sp-X)_n$,

35 3. A thermochromic polymerizable mesogenic composition
according to claim 1 or 2, characterized in that the chiral

polymerizable compounds of component MB are selected of formula III



in which

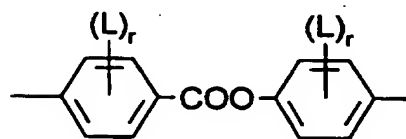
P, Sp, X and n have the meanings given for formula I in claim 1,

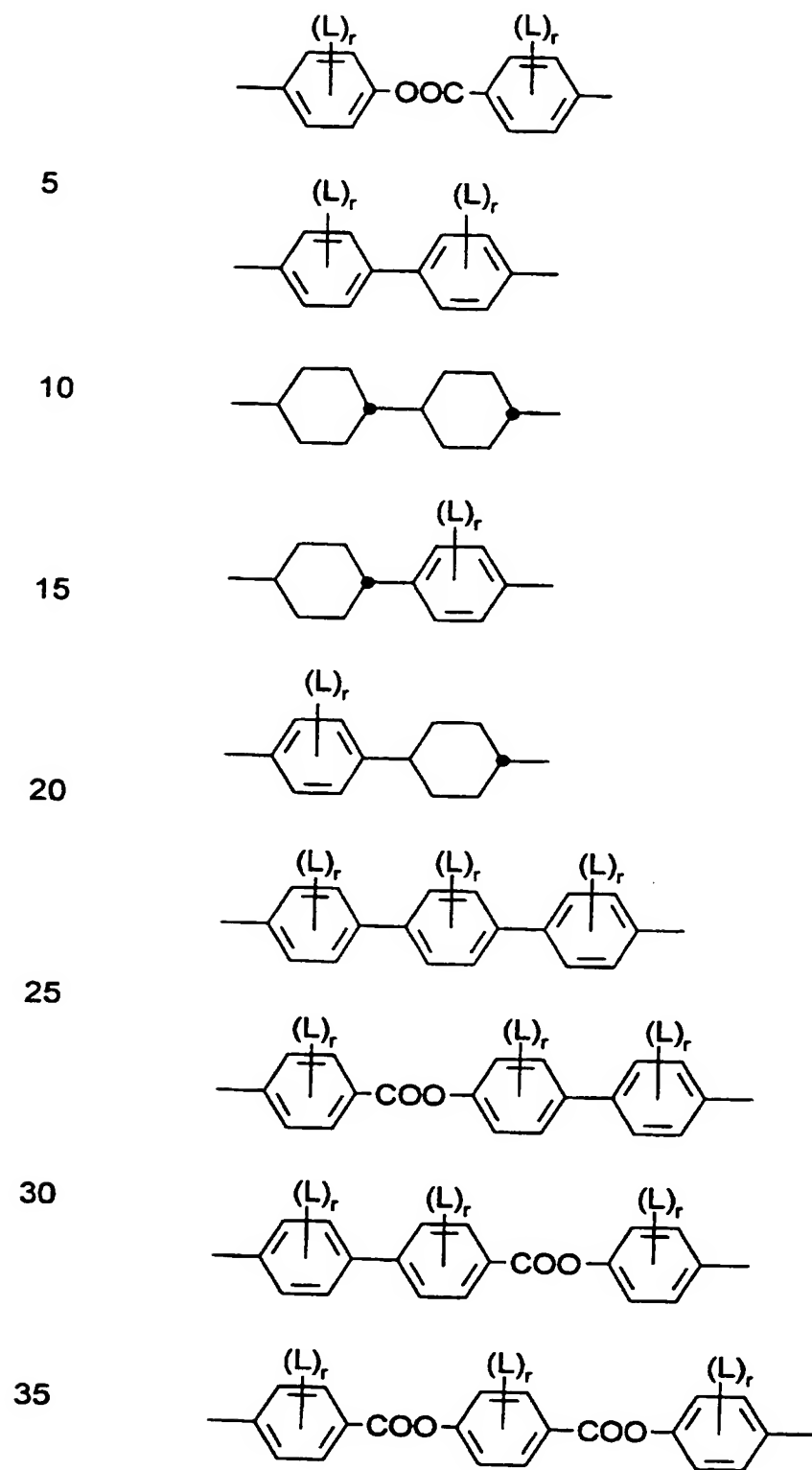
MG* is a mesogenic or mesogeneity supporting group, which is selected according to the formula II given in claim 1, and

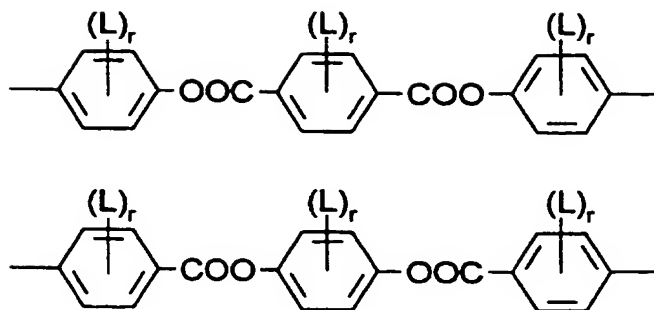
R* is H or an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or alternatively R* is halogen, cyano or has independently one of the meanings given for P-(Sp-X)_n.

wherein at least one of the groups MG* and R* is comprising at least one chiral structure element.

4. A thermochromic polymerizable mesogenic composition according to claim 2 or 3, characterized in that the mesogenic groups MG and/or MG* are selected, in each case independently, of the following formulae







5

10

wherein L in each case independently denotes halogen, a cyano or nitro group or an alkyl, alkoxy or alkanoyl group having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl, and r is 0, 1 or 2.

15

5. A thermochromic polymerizable mesogenic composition according to any of the claims 1 to 4, characterized in that it comprises at least one polymerizable mesogenic compound comprising two or more polymerizable functional groups.

20

6. An anisotropic polymer obtainable by polymerizing a thermochromic polymerizable mesogenic composition according to any of the claims 1 to 5.

25

7. A polymer film with a chiral mesophase and a helically twisted molecular structure that is obtainable by a process comprising the following steps

A) coating a thermochromic polymerizable mesogenic composition comprising

30

- a) a component MA comprising at least one achiral polymerizable mesogenic compound comprising at least one polymerizable functional group,
- b) a component MB comprising at least one chiral polymerizable mesogenic compound comprising at least one polymerizable functional group,

35

- c) a photoinitiator, and
d) optionally a dye component.
on a substrate or between two substrates in form of a layer,
- 5
- B) aligning the polymerizable mesogenic composition so that the axis of the molecular helix extends transversely to the layer,
C) heating at least a part of the aligned composition to a defined temperature,
- 10
- D) polymerizing at least a part of the aligned composition by exposure to actinic radiation,
E) optionally repeating step D) alone or together with step C) and /or steps A) and B) at least once, and
- 15
- F) optionally removing the substrate or, if present, one or two of the substrates from the polymerized material.
8. A polymer film with a chiral mesophase and a helically twisted molecular structure according to claim 7, wherein at least one part of the film exhibits a pitch of the molecular helix that is different from at least one other part of the film.
- 20
9. A polymer film according to claim 8 that exhibits at least two different reflection maxima in the visible wavelength range.
- 25
10. A process for preparing a polymer film with a chiral mesophase exhibiting a helically twisted molecular structure according to claim 7, 8 or 9, said process comprising the steps A) to F) as described in claim 7.
- 30
11. A process according to claim 10, wherein in step D) the thermochromic polymerizable mesogenic composition is covered at least partially with a photomask.
- 35
12. A process according to claim 11, wherein the photomask exhibits at least one part having a transmission of the actinic

radiation used in the polymerization step D) that is different from at least one other part of the photomask.

- 5
13. A process according to claim 10, 11 or 12, wherein step C) and D) are carried out at least two times, the defined temperature in at least one of the steps C) being different from the defined temperature in at least one other of the steps C).
- 10
14. Use of a thermochromic polymerizable mesogenic composition, an anisotropic polymer or polymer film with a chiral mesophase according to any of claims 1 to 9 for optical data storage, photomasks, decorative pigments, cosmetics, security applications, active and passive optical elements such as polarizers or optical retarders, colour filters, scattering displays, adhesives or synthetic
- 15
- resins with anisotropic mechanical properties.

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Application No: GB 9715766.3
Claims searched: 1-14

Examiner: Stephen Quick
Date of search: 17 October 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.O): C4X (X12)
Int Cl (Ed.6): C09K 19/46
Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB 2296807 A (SHARP), see pages 8 (lines 3-7) & 10 (lines 19-24)	-
A	EP 0661287 A1 (CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE), see pages 7 (lines 22-23) & 9 (lines 25-35); acknowledged in this application	-
X	WO 95/24454 A1 (BASF), see examples 55, 58, 59 & 62 for example (mixtures of both chiral & achiral polymerizable mesogenic compounds)	1-14

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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